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HIGH-RESOLUTION EPR AND PIEZOSPECTROSCOPY STUDIES OF THE LITHIUM-OXYGEN DONOR IN GERMANIUM

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Lithium-oxygen donors in germanium were studied at low concentration ($<10^{14}$ cm$^{-3}$) by means of Electron Paramagnetic Resonance and Photoelectric Piezospectroscopy. We find unambiguously four equivalent real-space positions with $<111>$ symmetry, which together with the four-valley conduction band lead to a 16-fold ground state. The system exhibits dynamic tunneling between the four equivalent orientations.

Lithium -- a technologically important impurity in germanium devices $^{1,2}$ -- has yielded results in IR Absorption$^3$ and Photoelectric Spectroscopy$^4$ experiments which have been controversial. The Li and Li-O donors in Si, on the other hand, $^{3,5}$ are well understood.

We have studied the Li-O-donor in Ge using improved EPR techniques and high-resolution Photoelectric Spectroscopy. The investigated Ge samples originated from ultra-pure single crystals $^6$ ($|N_A - N_D| < 10^{11}$ cm$^{-3}$) which were doped with lithium via diffusion at temperatures between 200°C and 400°C. The crystals contain typically $10^{14}$ oxygen atoms/cm$^3$.

The EPR studies were performed with a 24 GHz heterodyne spectrometer $^7$ at operating temperatures $\sim 2K$. Modes with $Q > 5 \cdot 10^5$, insensitive to tuning and extremely stable were used. As few as $10^{13}$ Li-O-donors could be observed with signal to noise ratio of $\sim 100$.

The spectrum for magnetic fields in the $(1\bar{1}0)$ plane consists of one double and two single lines. A typical experimental curve is shown in Figure 1. The g-factors for $\hat{H}_m$ $(1\bar{1}0)$ are shown in Figure 2. A theoretical fit to the data yields donors with $<111>$ type symmetry, and with $g_\perp = 1.9040\pm 0.0010$.

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Figure 1. Typical EPR spectrum of the Li-0 donor in Ge.

Attempts to saturate the Li-0 EPR lines failed due to ionization of the donors; this is seen by a rapid increase in the free-electron cyclotron line intensities. Under these circumstances ENDOR experiments are impossible.

Photoelectric piezospectroscopy was performed using a Fourier transform IR-spectrometer. High resolution was achieved by keeping the Li concentration below $10^{13}$ cm$^{-3}$. Figure 3 shows two spectra at $T = 6.5K$ with and without stress. Both spectra show "hydrogenic" character. A series of spectra at intermediate stress shows that the broad features at $\sim 62$ and $67$ cm$^{-1}$ in the zero stress spectrum develop continuously into the two sharp lines at

and $g_\parallel = 0.8585 \pm 0.0010$. 

Figure 2. The g-factors of the Li-0 donor in Ge.
Figure 3 (above, left). Photoelectric spectrum of the Li-0-donor in Ge at $T = 6.5K$.

-65 and 66 cm$^{-1}$ in the high stress limit. The sharp line at -70.5 cm$^{-1}$ does not change its position under stress.

The weak line at -67 cm$^{-1}$ at high stresses and its hydrogenic partners are the only ones due to free Li donors: they are very sensitive to total Li and O concentrations and they increase rapidly when $N_{Li} > N_{0}$. At low stresses the 67 cm$^{-1}$ line blends into Li-0 broad lines.

The EPR and IR spectra of Li-0 can be interpreted unambiguously in terms of donors with axial symmetry along <111> -- e.g. a diatomic complex oriented along <111> axes -- which tunnels between all four possible real space orientations.

Figure 4 (below, left). The energy levels of the Li-0-donor ground manifold as a function of stress. Degeneracy is shown by the number of dots.
Figure 4 shows the eigenvalues of the 16-fold ground-state multiplet as a function of stress. This degeneracy arises from the 4 real-space orientations and the 4-valley degeneracy of the Ge conduction band.

In summary we have observed an electronic effect caused by a dynamic tunneling of the nuclei of the Li-O complex. This model, including the high multiplicity and the tunneling, explains the puzzling features of previous work and eliminates the discrepancies found in the interpretation of the data.

References

6. Crystals grown at the Lawrence Berkeley Laboratory.
9. Compare this spectrum with the usual 4-fold multiplet as given by H. Fritzschke, Phys. Rev. 125, 1560 (1962).